



NRL/MR/6110--01-8584

# **Response of METS Sensor to Methane Concentrations Found on the Texas-Louisiana Shelf in the Gulf of Mexico**

R. A. LAMONTAGNE  
S. L. ROSE-PEHRSSON

*Chemical Dynamics and Diagnostics Branch  
Chemistry Division*

K. E. GRABOWSKI  
D. L. KNIES

*Surface Modification Branch  
Materials Science and Technology Division*

October 15, 2001

20011128 217

Approved for public release; distribution is unlimited.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE October 15, 2001		3. REPORT TYPE AND DATES COVERED Interim
4. TITLE AND SUBTITLE Response of METS Sensor to Methane Concentrations Found on the Texas-Louisiana Shelf in the Gulf of Mexico				5. FUNDING NUMBERS PE61153N
R.A. Lamontagne,* S.L. Rose-Pehrsson,* K.E. Grabowski,† and D.L. Knies†				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory 4555 Overlook Avenue, SW Washington, DC 20375-5320				8. PERFORMING ORGANIZATION REPORT NUMBER NRL/MR/6110--01-8584
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5660				10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES *Chemistry Division †Materials Science and Technology Division				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.				12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words)  A commercially produced solid state methane sensor (METS) from ASD Sensortechnik Gmgh (Germany) was used to obtain methane concentrations in sea water in the vicinity of methane hydrates. The use of semiconductor technology and membrane separation of methane (and other hydrocarbons) from the water column has been incorporated into the METS sensor. The response time is slow (minutes) and consequently complete equilibrium may never be reached depending upon the application of the sensor. The METS sensor was positioned on top of the forward platform of the Harbor Branch Oceanographic Institution's (HBOI) submersible, Johnson-Sea-Link I. This position enabled the sensor to be placed in the vicinity of methane hydrates. The Texas-Louisiana Shelf in the Gulf of Mexico was selected for investigation because of the existence of methane hydrates on the seafloor. The data reported here ranges from low nmol/l concentrations in no hydrate areas to umol/l concentrations in the vicinity of hydrates. Mussel beds and brine pools exhibited concentrations intermediate to these two extremes. Even though response and recover time of the sensor can be slow when encountering high methane concentrations, interesting detail was obtained on several of the dives.				
14. SUBJECT TERMS Methane Methane hydrates METS Dissolve methane concentration Gulf of Mexico Mussel beds Methane sensor Brine pools				15. NUMBER OF PAGES 13
				16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

## CONTENTS

INTRODUCTION .....	1
BACKGROUND .....	1
METHODS AND SENSOR PLACEMENT.....	3
RESULTS AND DISCUSSION.....	5
CONCLUSIONS .....	9
REFERENCES .....	9

# RESPONSE OF METS SENSOR TO METHANE CONCENTRATIONS FOUND ON THE TEXAS-LOUISIANA SHELF IN THE GULF OF MEXICO

## INTRODUCTION

The Naval Research Laboratory (NRL) is conducting a broadly based research program to study the dissociation and creation of methane hydrates, an ice like material composed of methane gas locked in a cage formed by water. The program is called an Accelerated Research Initiative (ARI). This denotes the Laboratory's belief that both a knowledge base and the technology exist at a level where major strides can be made in our understanding of the role of methane hydrates in the marine environment over the next five years.

From a geotechnical perspective, there is evidence that methane hydrates are associated with seafloor instability. From a geoacoustics perspective, there are indications that methane hydrates can produce acoustic scattering and acoustic propagation anomalies that could adversely impact Navy acoustic systems. Methane hydrates also represent a potential new source of energy, especially for countries that lack conventional hydrocarbon reserves

To increase our understanding of the role that methane hydrates play in the marine environment, NRL scientists have studied methane hydrates off the East Coast of the United States (Blake Ridge), on the Cascadia Margin (off Vancouver Island), in the Gulf of Mexico, and in the Nankai Trough off Japan. Methane hydrates are ubiquitous; current distribution maps show that they are found along most continental margins.

## BACKGROUND

The sensor portion of the NRL's methane hydrate ARI originally listed several potential options for sensor development. Subsequent approved funding levels allowed for only the implementation of one of these options. A commercially produced methane sensor, METS, from ASD Sensortechnik Gmgh (Germany) became commercially available at the start of the Methane Hydrate ARI. This sensor was purchased to acquire data while other sensing options were being explored. It was necessary to obtain a sensor since a cruise to the Gulf of Mexico using a submersible was planned for early summer 2000 (approximately 8 months after funding commenced).

The METS sensor specifications list an operational depth range from 0-2000 m, temperature range of 0-40 °C, and a methane concentration range of 50 nmol/l – 10 umol/l (actual range is < 20 nmol/l - >20 umol/l. The methane sensor is a semi-conductor (tin oxide) that works on the principle of hydrocarbon adsorption. This adsorption is on the active layer which leads to electron exchange with oxygen present. The subsequent

modification in the resistance results in a voltage change that is measured and recorded. The sensor cavity is separated from the seawater by a 5 micron thick silicone membrane. Support for this membrane is from a porous metal frit and a perforated metal plate. This allows for gas diffusion to the sensors to take place. The membrane allows diffusion of dissolved gases from the surrounding seawater into the sensor cavity. The diffusion is concentration gradient driven (Henry's Law). A humidity sensor is co-located with the methane sensor in the sensing cavity behind the membrane. The sensor is powered from a 9-36 volt DC supply. On average, the sensor has a current consumption of 230 mA.

Three sensors were purchased from ASD (D12, D21 and D23). The electronics were the same between D12 and D21/23, but the physical size was very different (Figure 1).



Figure 1. METS sensor D23 located on left, D12 located to the right.

The later two sensors (D21/23) were approximately 50% smaller than D12 and commensurately lighter. The membrane size was the same for all the sensors but the exposed surface area for D21/D23 is approximately 35% greater than for D12. The methane and humidity sensors were also the same size. D12 was received in time to perform preliminary laboratory experiments (fresh and seawater) and to become familiar with the operation of the sensor. D21/23 were received prior to the cruise. They were tested for proper response. Both sensors were responsive to various methane concentrations. None of the sensors were field tested prior to the summer cruise.

Sensors D21 and D23 were deployed on the Gulf of Mexico field study. Both D21 and D23 tested in the laboratory appeared more reliable than D12. However, once deployed

in the field experiments, it became apparent that D21 had an intermittent data collection problem when using power from the submersible. Sensor D23 was rendered inoperable by a power surge.

## METHODS AND SENSOR PLACEMENT

Originally the METS sensor was located on a vertical pole located on the port side of the observation bubble. It was below one of the vertical thrusters (Figure 2). The membrane surface was in the downward position.

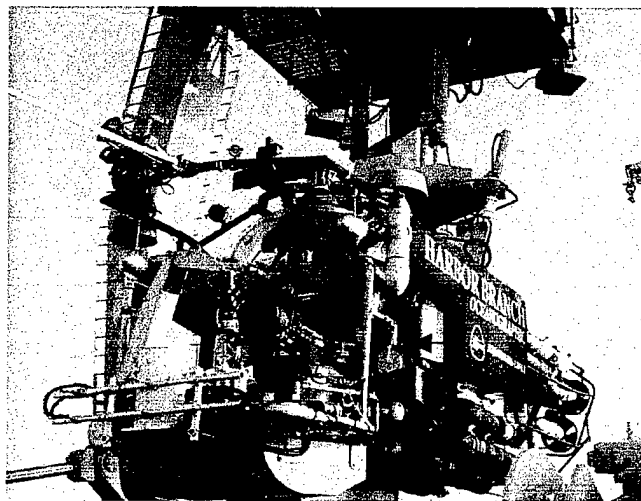


Figure 2. Original placement of METS sensor on vertical pole below thruster (red arrow).

There is a slight depression in the sensor face where the membrane is located. In this inverted position, bubbles can become trapped against the membrane leading to erroneous readings. When the submersible was ready to return to the surface after dive 1, the ballast tanks were blown and a large gas bubble along with indications of oil which had seeped from the bottom and collected in the ballast chamber were discharged onto the METS sensor. A very large peak was observed ( $\sim 22$   $\mu\text{mols/l}$ ). The peak decayed relatively quickly but a second large peak of approximately the same concentration was observed when the ballast tank was again blown (Figure 3). Because of these conditions, the sensor was relocated to its present position. There were few interesting details to observe on the first dive. Problems with the power source and software became apparent on this first dive. Much of the earlier part of the dive was lost.

The two very large peaks decayed reasonably fast after the ballast discharges. The term "reasonable decay of the methane peaks" must be placed in the context that the methane is oxidized only when there is sufficient oxygen present to facilitate the oxidation. The oxygen must also diffusive across the same membrane as the methane. The rapid decay of the methane peak indicates that the bottom water in which the dive took place is well oxygenated.

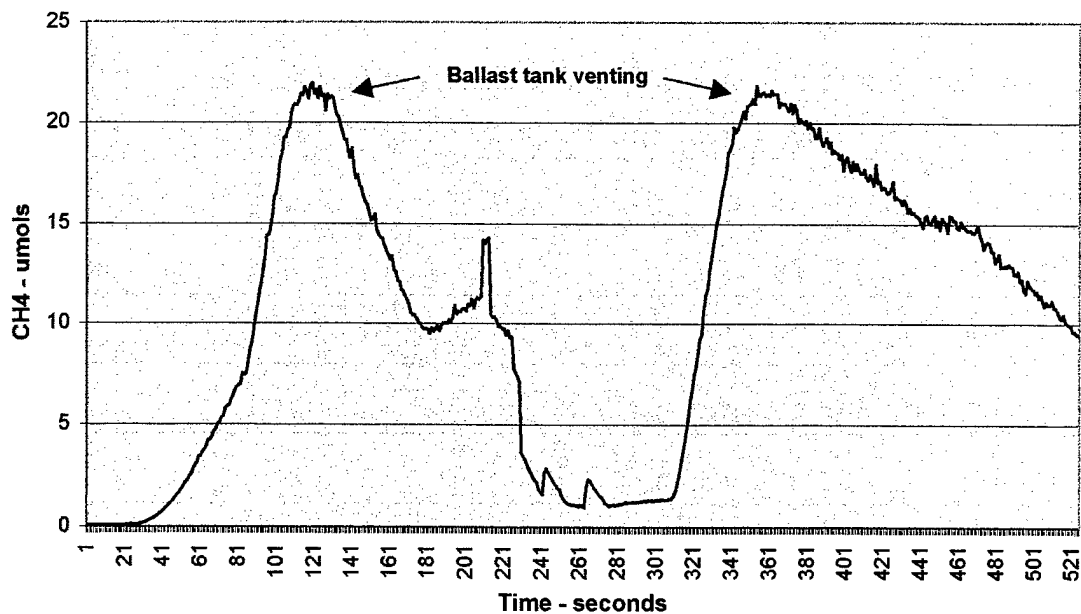


Figure 3. Results of ballast tank (gas and oil) being blown onto the METS sensor.

Upon retrieval to the deck, it was apparent the membrane was darkened with oil and needed to be replaced. Upon changing the membrane, it was noticed that the sensors in the sensor cavity had been displaced backward into the electronics compartment (Figure 4).

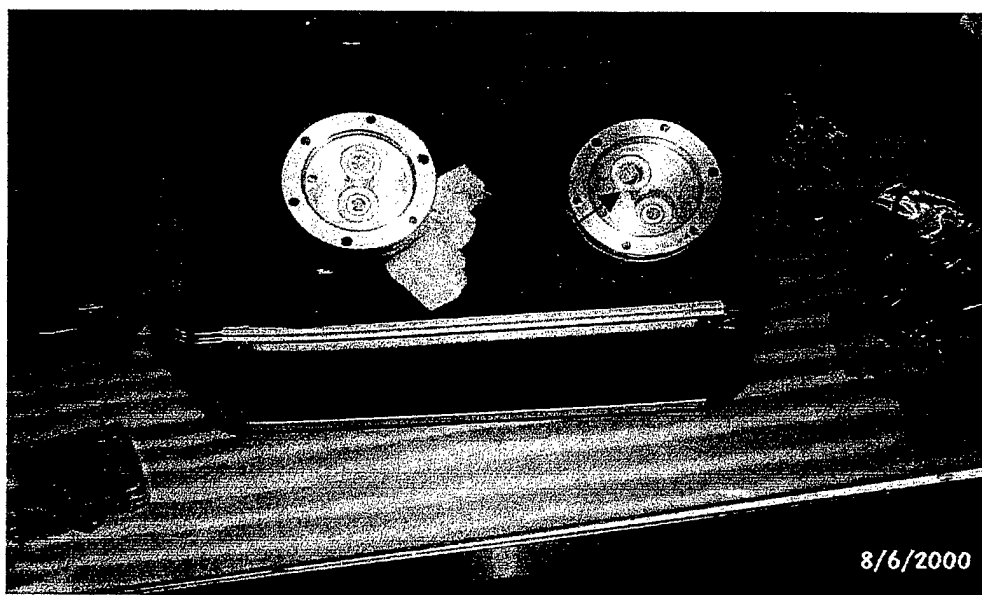


Figure 4. Displacement of sensors into electronics compartment (red arrow).

The sensors were placed in their original position and the sensor was used in this configuration for the duration of the cruise. At this time the location of the sensor was also changed. The METS sensor subsequently was placed on the forward platform in view of the submersible driver (Figure 5). This allowed for the operator in the front compartment to observe where the sensor was located in relation to the activities taking place.

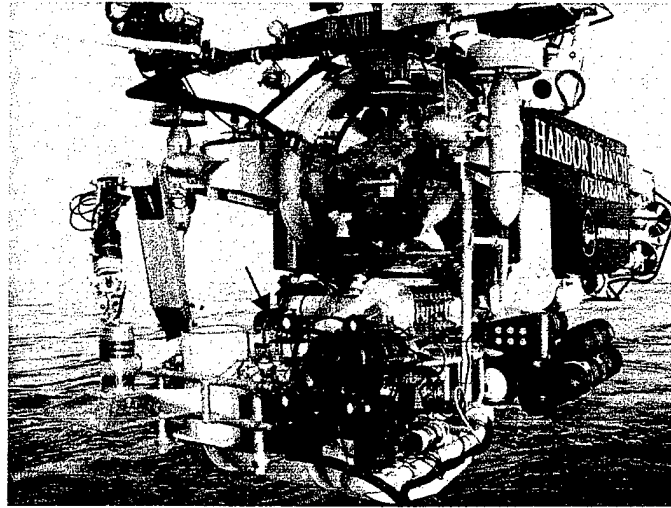


Figure 5. Placement of METS sensor in view of submersible operator (red arrow).

It was during the first dive that the software problem(s) manifested itself. The sensor would erratically stop taking data after it had been started. Often it would be difficult to restart. Information obtained from ASD indicated that not all the METS units produced appeared to have this software malfunction. A correction of the software was being prepared at the time of the cruise. Also, information from ASD stated that our problem with the sensor displacement into the electronics compartment was the first time that this has been reported. It appears that there were multiple problems with deployment of the METS sensor not only with the original physical location of the sensor but also with the software and internal physical alignments.

## RESULTS AND DISCUSSION

The software problem was exacerbated with the power transients that were associated with the submersible's power supply. The loss of power to the unit required multiple start-ups during a dive. This combined with rotating operators whose dive mission were another project(s), left the data log of activities associated with the METS sensor poorly annotated. Thus, only those dives, which were properly documented, will be presented and discussed. Figure 6 shows the areas that were sampled during the cruise to the Gulf of Mexico. Table 1 indicates station (figures) location described in text below.



## Outcropping Hydrate Sites

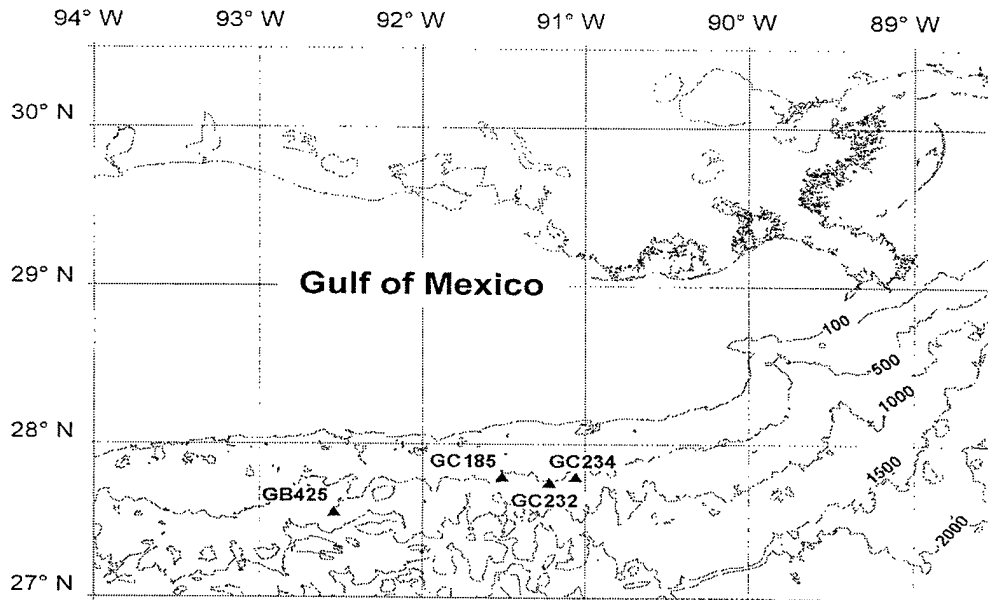


Figure 6. Areas are indicated where sampling (water and cores) were accomplished.

SITE LOCATIONS	FIGURES		
	3	7	11
GC 185			
GC232	10		
GC234	8	9	

Table 1. Location of figures (described below) on site map in Figure 6.

Figure 7 has numerous peaks, however, the maximum peak on this dive is only 0.4 umols/l. The first peak located at approximately 6,274 seconds ( $\sim 0.22$  umols/l) was obtained in the vicinity of small hydrate and an orange mat (bacterial?) associated with it. The second peak at 7,265 seconds is associated with 2/3 small pieces of hydrate. The final peak at 9,884 seconds is associated with a large piece of hydrate. As can be seen from this plot, it is difficult to associate pieces of hydrates with the concentrations obtained by the METS sensor at this particular location.

Figure 8 shows data collected while working with hydrate mounds or with pieces of hydrate. Methane concentrations rise from a background level of  $\sim 0.1$  umols/l to a high of  $\sim 8.8$  umols/l. The first peak ( $\sim 2.1$  umols/l) at 5,788 seconds was obtained when working around a loose piece of hydrate. While working a hydrate mound at 6,634 seconds, a concentration of  $\sim 2.9$  umols/l was obtained. The highest concentration ( $\sim 9$  umols/l) occurred while cores were being taken in a hydrate mound. The peak located at 10,523 seconds occurred while working in a mussel bed located to the left of the hydrate mound.

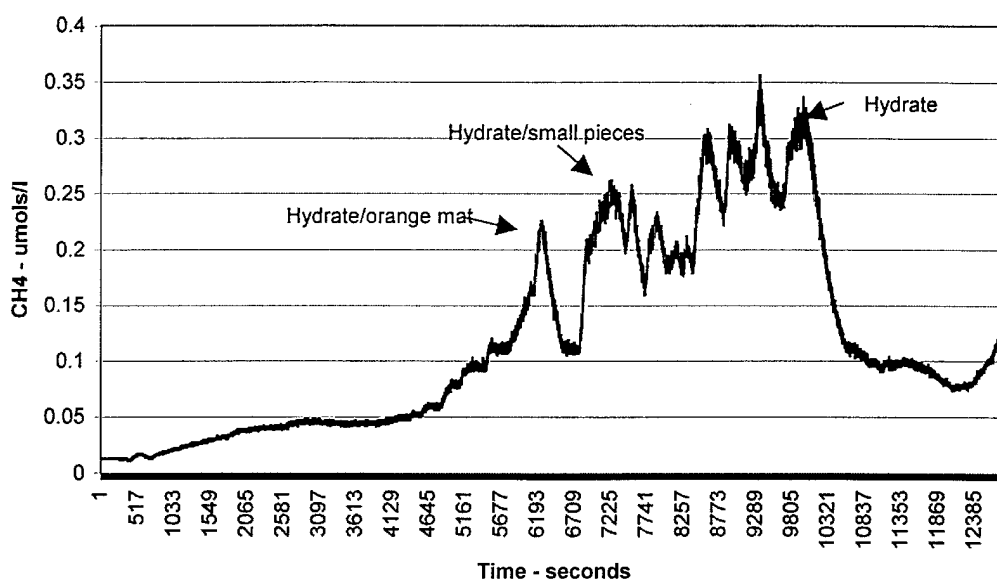


Figure 7. This graph shows methane (plus hydrocarbons) concentrations in the vicinity of hydrates. Methane levels in open ocean conditions should be  $\sim 0.004$  umols/l.

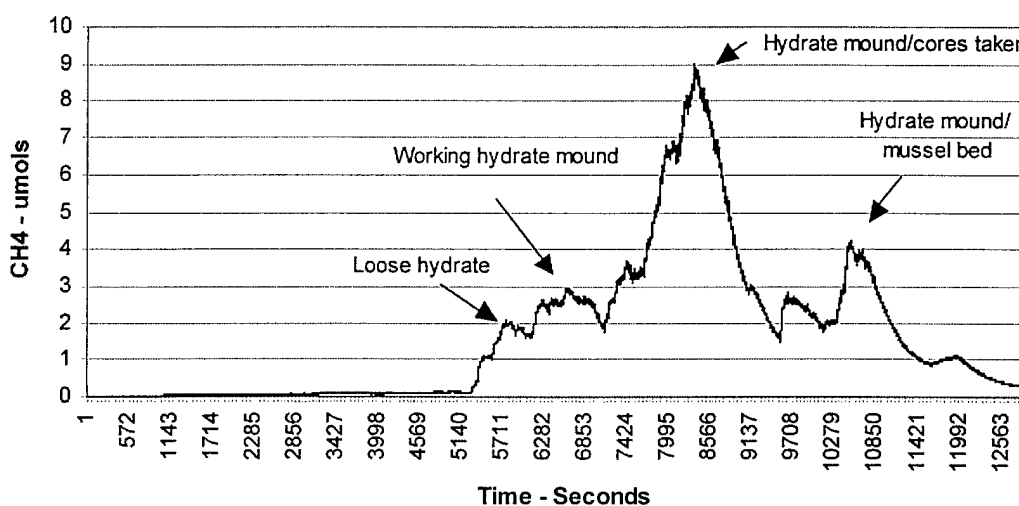


Figure 8. This plot shows that high methane concentrations can be observed in the vicinity of hydrate outcroppings.

Figure 9 has subdued detail except for one peak ( $\sim 3.1$  umols/l) at approximately 9,000 seconds. The submersible had stirred up the bottom sediment and was waiting for the sediment to settle down before collecting more hydrate samples. The peak decay was initiated by purging the sensor with ballast air after moving away from the bottom while attempting to retrieving some floating hydrates. The sharp dip in the methane profile at 13,633 seconds indicates that the submersible has been hoisted from the water. It was

found that purging the sensor with ballast air would help it recover more quickly than by the normal procedure of oxygen diffusion from seawater.

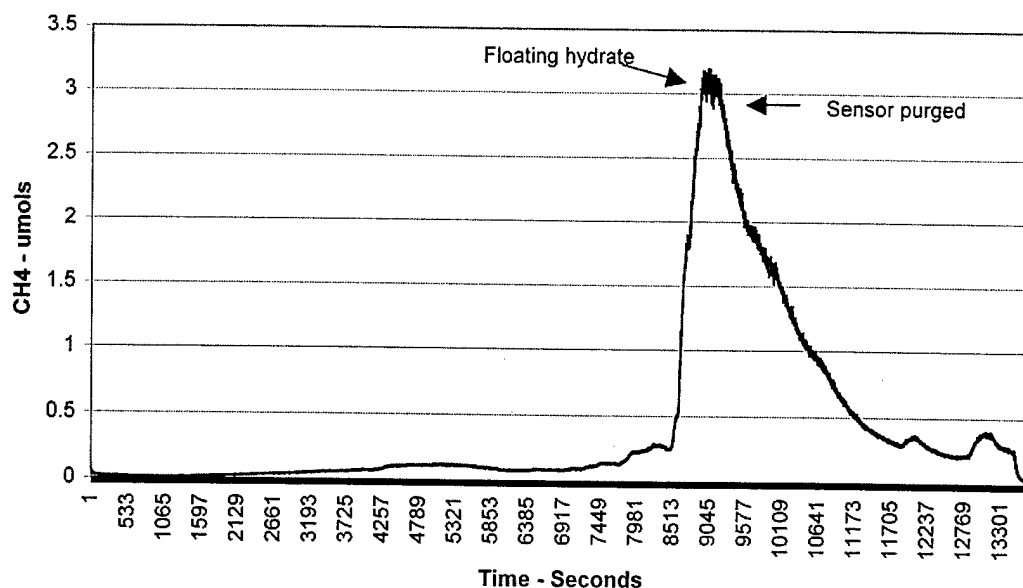


Figure 9. Graph showing results of using ballast air to speed recovery of METS sensor.

Figure 10 is a departure from the single peak dive in figure 9. In this dive, there are multiple peaks, which are slightly but significantly elevated from bottom background levels. The first plateau occurs at 2,272 seconds when the submersible reaches the bottom. The methane concentration is  $\sim 0.05$  umols/l. The first peak at 3,664 seconds

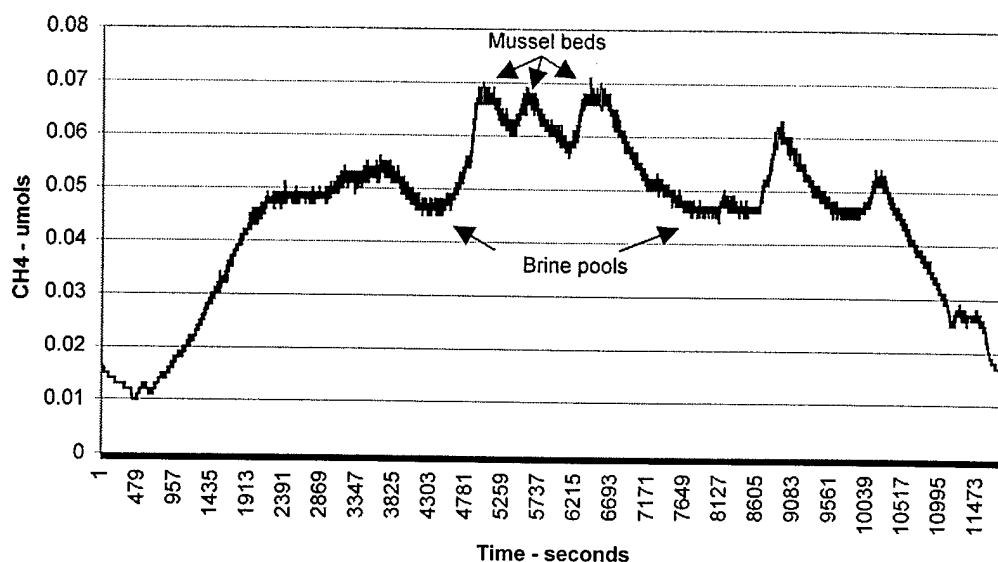


Figure 10. An example of low methane concentrations with strong local variability.

has a concentration of 0.06 umols/l and is located just prior to a brine pool. There is a decrease in the concentration to  $\sim 0.045$  umols/l as the submersible passes over the brine

pool. The next three peaks, all with an approximate methane concentration of 0.07  $\mu\text{mol}/\text{l}$ , are located by/over mussel beds. Methane concentrations once again decrease to 0.045  $\mu\text{mol}/\text{l}$  over the brine pool. The peak at 8,900 seconds was not identified in the logs. The last peak occurred when the submersible was leaving the bottom. There is the possibility that the bottom was stirred and resulted in a slight increase in the methane concentration. The short plateau and then sudden dip in the methane concentration are the result of the submersible reaching the surface and then being hoisted out of the water.

Figure 11 had little log information for association with the methane profile. Compared to the maximum concentration found in figure 10 of 0.07  $\mu\text{mol}/\text{l}$ , the concentrations in this location are orders of magnitude higher, 5  $\mu\text{mol}/\text{l}$ . The information that is available indicates that the submersible is entering the lower scattering layer at approximately 3,300 seconds and the visual conformation of bubbles rising from the sea floor at approximately 4,000 seconds. Methane concentrations start to rise shortly after confirmation of rising bubbles. The maximum concentration is obtained at 7,600 seconds when the submersible reaches the ocean floor. Bubbles rising from the sea floor have a marked influence on the ambient dissolved methane concentration. No mention is made of bubbles rising from the sea floor in dive 4222 (figure 10) and the ambient methane concentration is between 0.05 and 0.07  $\mu\text{mol}/\text{l}$ .

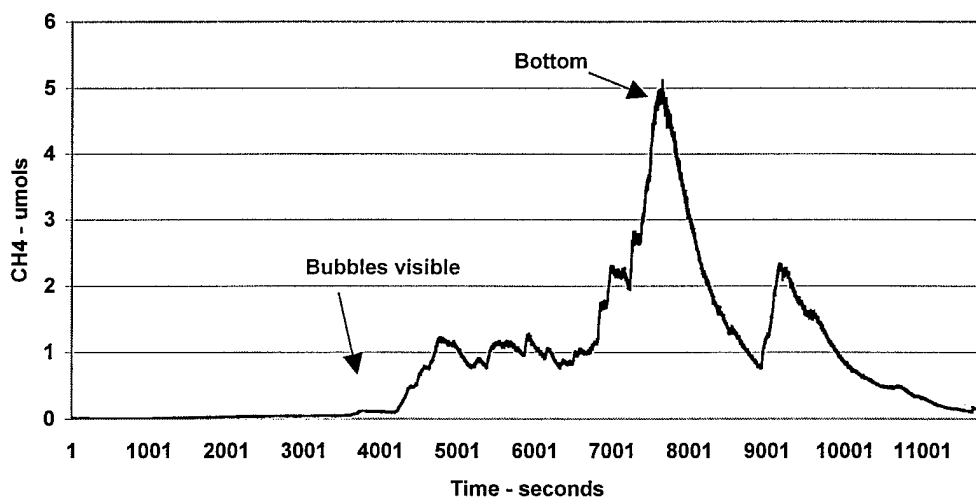


Figure 11. Influence of bubbles on the ambient dissolved methane concentration.

## CONCLUSIONS

From the data presently available, there are “cause and effect” correlations between the presence of methane hydrates and dissolved methane concentrations in seawater. When samples were being retrieved from exposed methane hydrate mounds, the dissolved concentrations in the water column were always higher (in some cases orders of magnitude higher). It is not possible at this time to absolutely correlate the dissolved methane concentration in seawater with exposed hydrates. The METS membrane is not specific for methane. The membrane will pass all low-molecular weight hydrocarbons (up to four carbon atoms in size) and the sensor will respond to these hydrocarbons.

Thus the signal could be from methane or a combination of several hydrocarbons. In the Gulf of Mexico, the probability of a mixture of these hydrocarbons is extremely high. Gas chromatography analysis of some of the water samples collected in the Gulf of Mexico at this time indicated that methane makes up approximately 65% of the signal while the rest of the signal is comprised of ethane, ethylene, propane, propylene and some four carbon based compounds. The presence of gas (methane?) seeps in the form of "gas bubbles" in the vicinity of methane hydrates contributes to the dissolved methane concentration in the water column. Particularly in the Gulf of Mexico, there are petroleum seeps (oil) which contain some methane (very small percentages of gas in the oil have an effect) and have an effect on the dissolved methane concentration. Much more work needs to be performed before useful correlations can be established between sensor response and hydrocarbon concentrations.